

Electrophilic Additions to Diphosphenes (RP=PR)

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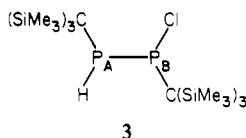
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The deployment of ligands with large steric bulk has permitted the recent isolation of compounds with Si=Si,¹ Ge=Ge,² Sn=Sn,³ and P=P⁴ double bonds. However, despite the considerable progress made in the synthesis of these novel species, relatively little is known about their reactivities.⁵ We report (i) that diphosphenes undergo facile electrophilic attack, (ii) differences in the reactivities of alkyl- and aryl-substituted diphosphenes (Me₃Si)₃CP=PC(SiMe₃)₃ (**1**) and (2,4,6-(*t*-Bu)₃C₆H₂)P=P-(2,4,6-(*t*-Bu)₃C₆H₂) (**2**), and (iii) an X-ray crystal structure determination of **1**.

Treatment of a solution of **1** in Et₂O at -20 °C with an equimolar quantity of dry, gaseous HCl led to fading of the yellow-orange color and the formation of the white solid [(SiMe₃)₃CP(H)P(Cl)C(SiMe₃)₃] (**3**). The high-resolution mass



spectrum (HRMS) for **3** showed the following (M⁺): calcd 560.2081, found 560.2095. The 32.38-MHz ³¹P{¹H} NMR spectrum of **3** exhibited two AX patterns of unequal intensity. For the more intense spectrum, (**3A**): δ_{P_A} -36.7 (d, ¹J_{PP} = 224.7 Hz), δ_{P_B} 173.6 (d, ¹J_{PP} = 224.7 Hz). For the less intense spectrum, (**3B**): δ_{P_A} -29.4 (d, ¹J_{PP} = 380.8 Hz), δ_{P_B} 154.1 (d, ¹J_{PP} = 380.8 Hz). The following ¹H couplings were obtained from the ¹H-coupled ³¹P spectrum, **3A** ¹J_{PAH} = 201.6 Hz, ²J_{PBH} = 26.7 Hz; **3B**, ¹J_{PAH} = 213.9 Hz, ²J_{PBH} = 25.3 Hz. Treatment of **1** with an excess of gaseous HCl in Et₂O resulted in cleavage of the phosphorus-phosphorus bond and formation of [(Me₃Si)₃CP(H)Cl] (**4**). The HRMS for **4** showed the following (M⁺): calcd 298.0924, found 298.0933. ³¹P NMR δ 70.5 (d, ¹J_{PH} = 160.6 Hz). It was not possible to isolate a product analogous to **3** when **2** was treated with an equimolar quantity of HCl at -78 °C. Instead, complete P=P bond cleavage was observed resulting in [(2,4,6-(*t*-Bu)₃C₆H₂)P(H)Cl] (**5**). The HRMS for the M - 1 peak of **5** showed the following: calcd 311.1695, found 311.1691. ³¹P NMR δ 26.4 (d, ¹J_{PH} = 215.0 Hz). Phosphines of the type RP(H)(halogen) are remarkable because they are normally unstable.⁶

(1) (a) West, R.; Fink, M. J.; Michl, J. *Science* (Washington, D.C.) **1981**, 214, 1343. (b) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, 104, 1150. (c) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *Ibid.* **1982**, 104, 4992.

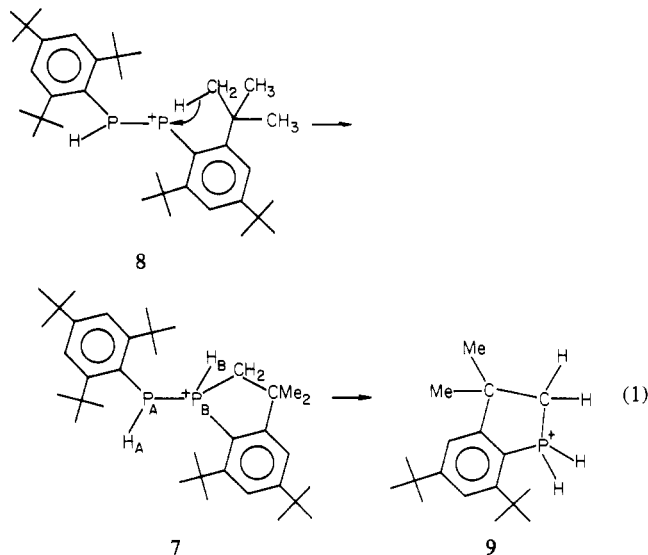
(2) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, 104, 6136.

(3) For a discussion of the bonding in the [(Me₃Si)₂CH]₂Sn, see: Fjeldberg, T.; Haaland, A.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1407, and references therein.

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(5) For a preliminary account of the reactivity of (mes)₂Si=Si(mes)₂(mes = mesityl) see: Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, 105, 1070.

Differences in the reactivity of **1** and **2** were also apparent from protonation studies using HBF₄·Et₂O. Treatment of **1** with excess HBF₄·Et₂O in CH₂Cl₂ at -78 °C for 2 h produced [(Me₃Si)₃CPH₃][BF₄] (**6**). ³¹P NMR data for **6**: δ -56.3 (q, ¹J_{PH} = 502.2 Hz). Protonation of **2** with excess HBF₄·Et₂O in CH₂Cl₂ solution at -78 °C resulted initially in a compound (**7**) with an AX ³¹P{¹H} NMR spectrum (36.43 MHz). The corresponding ¹H-coupled ³¹P spectrum (-50 °C) showed additional coupling, thus indicating the attachment of one hydrogen to each phosphorus plus additional fine structure relating to P_B: δ_{P_A} -86.1 (ddd, ¹J_{PP} = 290 Hz, ¹J_{PAH_A} = 229.0 Hz, ²J_{PAH_B} = 6.6 Hz), δ_{P_B} 10.6 (ddd, ¹J_{PP} = 290 Hz, ¹J_{PBH_B} = 481 Hz, ²J_{PBH_A} = 9.8 Hz). On the basis of these data we propose the structure shown in eq 1 for **7**. We



propose further that **7** arises via intramolecular C-H oxidative addition of an initially formed two-coordinate phosphorus cation, **8**.⁷ Warming of a solution of **2** in HBF₄·Et₂O resulted in P-P bond cleavage and the formation of **9**: ³¹P{¹H}NMR δ 17.7 (t, ¹J_{PH} = 528 Hz).

An X-ray crystallographic study of **1** was undertaken⁸ because of the differences in reactivity of **1** and **2**.⁹ There are two crystallographically independent molecules (A and B) in the asymmetric unit, and each contains a crystallographic center of inversion at the midpoint of the P=P bond (Figure 1). The phosphorus-phosphorus bond length in molecule A is 2.014 (6) Å while that in molecule B is 2.004 (6) Å; cf. 2.034 (2) Å in **2**.^{4a} The P-P-C angles in **1** are approximately 6° wider than those

(6) the only exception is when R=CF₃ (Dobbie, R. C.; Goshij, P. D.; Straughan, B. P. *J. Chem. Soc., Dalton Trans.* **1975**, 2368) or when RP(H)(halogen) is coordinated to a transition metal: Marinetti, A.; Mathey, F. *Organometallics* **1982**, 1, 1488 and references therein.

(7) Previously we have demonstrated that two-coordinate phosphonium cations undergo C-H oxidative addition reactions. See: (a) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, 104, 3239. (b) Cowley, A. H.; Mehrotra, S. K. *Ibid.* **1983**, 105, 2074. For ring closures of 2,4,6-(*t*-Bu)₃C₆H₂-phosphorus compounds, see: (c) Bacciero, A.; Bertrand, G.; Mazerolles, P.; Majoral, J.-P. *J. Chem. Soc., Chem. Commun.* **1981**, 1197. (d) Yoshifuji, M.; Shima, I.; Ando, K.; Inamoto, N. *Tetrahedron Lett.* **1983**, 24, 933.

(8) A crystal of dimensions 1.0 × 0.6 × 0.3 mm was sealed under dry nitrogen in a Lindemann capillary and mounted on an Enraf-Nonius CAD-4 automated diffractometer. A total of 2275 reflections were measured to 2θ max of 36° by using Mo Kα radiation (λ 0.71069 Å) and a graphite monochromator. Of these 2046 reflections were considered observed. Compound **1** crystallizes in the triclinic space group P1 with Z = 4. The unit-cell dimensions are a = 16.629 (7) Å, b = 9.155 (5) Å, c = 12.482 (6) Å, α = 91.58 (4)°, β = 111.42 (5)°, γ = 90.02 (4)°. No absorption or extinction corrections were applied. The structure was solved by direct methods using the SHELX program system. The final R and R_w values were 0.086 and 0.086. Tables of atomic coordinates, thermal parameters, bond lengths and bond angles are available as supplementary material.

(9) After the submission of this paper two reports on the reactivity of diphosphenes have appeared: (a) Niecke, E.; Rüger, R. *Angew Chem., Int. Ed. Engl.* **1983**, 22, 155. (b) Yoshifuji, M.; Ando, K.; Toyota, K.; Shima, I.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 419.

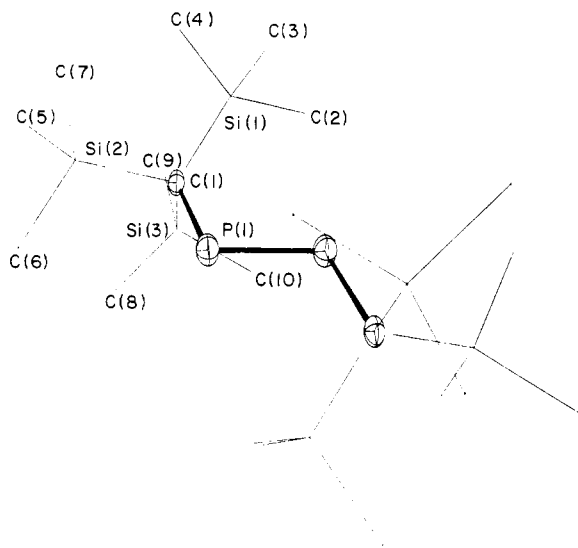


Figure 1. View of $(\text{Me}_3\text{Si})_3\text{CP}=\text{PC}(\text{SiMe}_3)_3$ (**1**) showing the atom numbering scheme. Pertinent metric parameters for molecule A: $\text{P}(1)-\text{P}(1') 2.014(6)$, $\text{P}(1)-\text{C}(1) 1.85(1) \text{ \AA}$; $\angle \text{P}(1')-\text{P}(1)-\text{C}(1) 108.2(4)^\circ$. For molecule B: $\text{P}(1)-\text{P}(1') 2.004(6)$, $\text{P}(1)-\text{C}(1) 1.87(1) \text{ \AA}$; $\angle \text{P}(1')-\text{P}(1)-\text{C}(1) 108.9(4)^\circ$.

in **2**, presumably as a result of the larger size of $(\text{Me}_3\text{Si})_3\text{C}$ over $(2,4,6\text{-}t\text{-Bu})_3\text{C}_6\text{H}_2$. We suggest that this difference in ligand size is responsible for the stability of the HCl addition product **3** and the absence of a corresponding product from the reaction of **2** with HCl.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (4 pages). Ordering information is given on any current masthead page.

Vinyl Hydrogen Activation in Mono- and Dinuclear $(\eta^5\text{-Cyclopentadienyl})(\text{hexatriene})\text{cobalt}$ Complexes. Thermal and Photochemical Hydrogen Shifts of Complementary Stereochemistry

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The activation of C-H bonds in hydrocarbons by soluble transition-metal complexes has been the focus of intensive recent research.¹ Its vinyl variant has been relatively unexplored,² having

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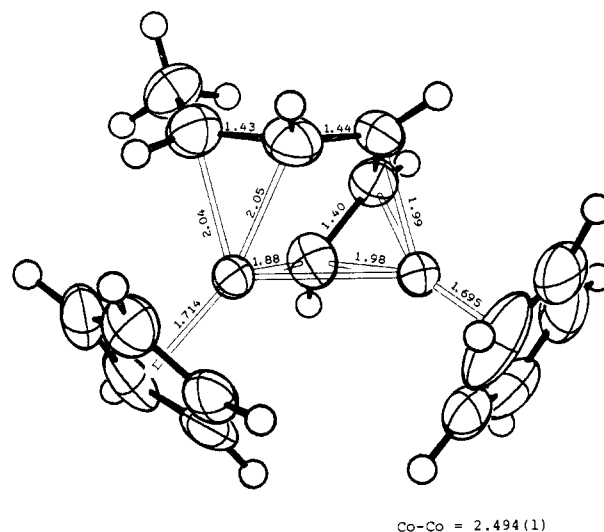
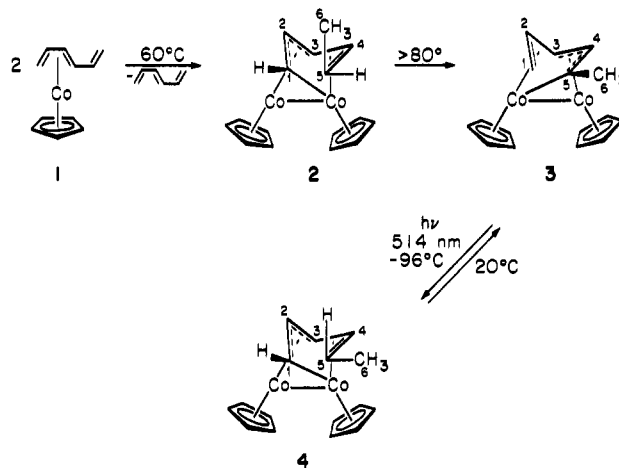


Figure 1. ORTEP drawing of **2** including selected bond lengths (angstroms). Ellipsoids are scaled to represent 50% probability surface. The hydrogen positions shown are those calculated on the basis of idealized geometry following their locations on the difference Fourier electron density map.

Scheme I



frequently been restricted to low-yielding complex cluster reactions.³ It also suffers from little mechanistic understanding. This is surprising, considering the ready availability of alkenes such

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(3) See, for example: (a) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2017-2020. (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Will, G. J.; McPartlin, M.; Nelson, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1190-1191. (c) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *Ibid.* **1980**, 547-549. (d) Bhaduri, S.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Raithby, P. R.; Rehani, S.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1979**, 562-568. (e) Ferrari, R. P.; Vaglio, G. A. *J. Organomet. Chem.* **1979**, *182*, 245-249. (f) Pierpont, C. G.; Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 616-618. (g) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Rehani, S. K. *J. Organomet. Chem.* **1976**, *113*, C42-C44. (h) Deeming, A. J.; Hasso, S.; Underhill, M. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1614-1620. (i) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29-C31. (j) Deeming, A. J.; Underhill, M. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1415-1419.